BIOMATERIALS

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PHASE FORMATION AND SINTERING OF HYDROXYAPATITE – FLUORITE COMPOSITIONS WITH ALKALI-CONTAINING ADDITIVES

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The main difficulty in fabricating ceramic materials based on hydroxyapatite is their high sintering temperature. Potassium feldspars, low-melting leucite glass, and synthetic alkali-containing compounds were investigated as compounds that increase the amount of melt for improving the sintering process. The effect of alkali-containing compounds on phase-formation processes occurring during sintering of compositions based on hydroxyapatite – fluorite mixtures is examined.

Glass ceramic materials based on hydroxyapatite (HA) are widely used in reconstructive medicine, jaw-facial surgery, and stomatology for making coatings for metallic implants or as wholly ceramic fragments for replacing damaged sections of bone. The main difficulty in making coatings and articles from HA is that this is a high-melting compound — the melting temperature of HA is about 1350°C.

The objective of our investigations is to determine the effect of alkali-containing additives on phase-formation processes occurring during sintering of compositions based on hydroxyapatite-fluorite mixtures.

It is known that to increase the mechanical indicators and decrease the porosity HA samples can be strengthened with, for example, glass. Silicon oxide, a component of glass, together with phosphorus ions can form a chemical bond with bone tissue [1]. Sodium, potassium, and lithium oxides present in glass increase the amount of melt in the system, which decreases the sintering temperature of the material. The use of feldspar (leucite) glass as the matrix makes it possible to obtain a material with total porosity of about 45%, pore size of the order of 500 μm, and bending and compression strengths 4.7 – 12.6 and 12.8 – 18.0 MPa, respectively [2].

Low-melting leucite glass, natural silicate compounds — potassium feldspars (PF), as well as synthetic alkali-containing compounds, used in making leucite glass and improving its properties — $Na_2B_4O_7 \cdot 10H_2O$, sodium dihydrophosphate $NaH_2PO_4 \cdot 2H_2O$, lithium fluoride LiF, and lithium hydroxide LiOH [3, 4] — were used as the compounds which decrease the sintering temperature of HA. Pure HA in a mixture with fluorite CaF_2 (the fluorite content in the mixtures reached 15%[2]) was used as a base for the compositions. The powder mixtures were pressed into 10 mm in diameter pellets and sintered in an electric furnace at 1200 – 1250°C in air. The compositions of are presented in Table 1.

In investigations of the products of sintering of hydroxyapatite – fluorite mixtures (compositions 1 – 5) close in composition to natural bone, XPA showed a change of the intensity of the x-ray reflections of different compounds with increasing CaF_2 content in the initial charge. For example, the structure HA was observed to improve and the intensity of the reflections of calcium phosphate decreased with increasing fluorite content in the charge (Fig. 1). The change in the intensity of the x-ray reflections of fluorapatite was negligible. After being heated to 1200°C the samples were porous, loose, and low-strength.

Since a melt was not attained in charges with the hydroxyapatite – fluorite composition at the sintering temperatures used, a third component — potassium feldspar — was added in the amount 7% (compositions 6 – 9) to decrease the melting temperature. The fluorite content changed from 1 to 15%. XPA established that in such compositions the amount of leucite increases gradually with increasing CaF_2 content as a result of the decomposition of potassium feldspar; the intensity of the reflections form HA and fluorapatite decreases only negligibly. As a result of the interaction of HA and fluorite with the melt, formed when the feldspar decom-

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[2] Here and below: mass content.

TABLE 1.

Composition	Mass content, %							
	CaF_2	HA	PF	LiF_2	$Na_2B_4O_7 \cdot 10H_2O$	$NaH_2PO_4 \cdot 2H_2O$	leucite glass	LiOH
1	1.0	99.0	–	–	–	–	–	–
2	5.0	95.0	–	–	–	–	–	–
3	7.5	92.5	–	–	–	–	–	–
4	10.0	90.0	–	–	–	–	–	–
5	15.0	85.0	–	–	–	–	–	–
6	8.5	84.5	7.0	–	–	–	–	–
7	10.0	83.0	7.0	–	–	–	–	–
8	12.5	80.5	7.0	–	–	–	–	–
9	15.0	78.0	7.0	–	–	–	–	–
10	7.5	66.5	25.0	–	1.0	–	–	–
11	7.5	65.5	25.0	–	2.0	–	–	–
12	7.5	63.5	25.0	–	4.0	–	–	–
13	7.5	63.5	25.0	–	6.0	–	–	–
14	7.5	59.5	25.0	–	8.0	–	–	–
15	7.5	44.5	25.0	–	12.0	–	–	–
16	7.5	51.5	25.0	–	16.0	–	–	–
17	7.5	66.5	25.0	1.0	–	–	–	–
18	7.5	65.5	25.0	2.0	–	–	–	–
19	7.5	63.5	25.0	4.0	–	–	–	–
20	–	99.0	–	–	–	1.0	–	–
21	–	97.5	–	–	–	2.5	–	–
22	–	95.0	–	–	–	5.0	–	–
23	–	92.5	–	–	–	7.5	–	–
24	–	90.0	–	–	–	10.0	–	–
25	–	99.0	–	–	–	–	1.0	–
26	–	97.5	–	–	–	–	2.5	–
27	–	95.0	–	–	–	–	5.0	–
28	–	92.5	–	–	–	–	7.5	–
29	–	90.0	–	–	–	–	10.0	–
30	–	97.5	–	–	–	–	–	2.5
31	–	95.0	–	–	–	–	–	5.0
32	–	90.0	–	–	–	–	–	10.0
33	–	85.0	–	–	–	–	–	15.0
34	–	80.0	–	–	–	–	–	20.0
35	–	75.0	–	–	–	–	–	25.0

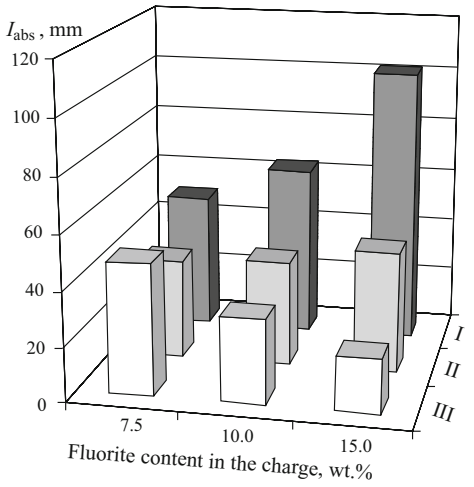

Fig. 1. Change of the intensity of x-ray reflections of different crystalline phases in the finished frit with the composition hydroxyapatite – fluorite with increasing CaF_2 content in the charge (compositions 1 – 3): I) HA (d = 0.281 nm); II) fluorapatite (d = 0.279 nm); III) calcium phosphate (d = 0.289 nm).

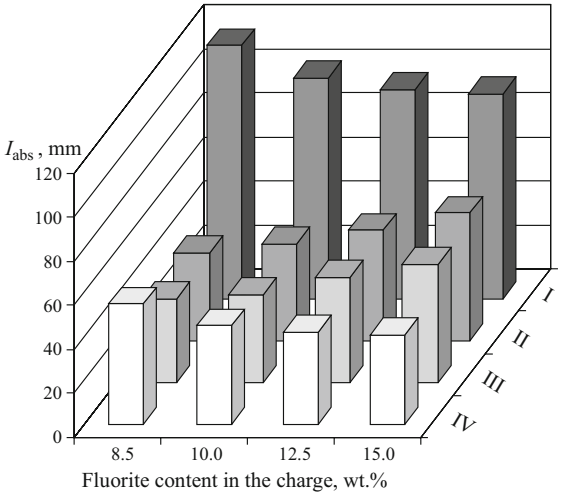

Fig. 2. Change of the intensity of x-ray reflections of different crystalline phases in the finished frit with the composition hydroxyapatite – fluorite – potassium feldspar as a function of the CaF_2 content in the charge (compositions 6 – 9): I) HA (d = 0.281 nm); II) leucite (d = 0.325 nm); III) wollastonite (d = 0.274 nm); IV) fluorapatite (d = 0.279 nm).

poses, wollastonite α-$CaO \cdot SiO_2$ appears in the system, and its amount increases with increasing content of fluorite in the charge (Fig. 2). In the samples made from such material, the shrinkage is small and the water absorption decreases with increasing temperature. Although the presence of leucite and wollastonite has a favorable effect on the mechanical properties of the finished ceramic, samples with such compositions are also extremely depleted of the glass phase, and they were modified by adding different fluxes.

When sodium tetraborate is added to the composition hydroxyapatite – potassium feldspar – fluorite (compositions 10 – 16), the x-ray reflections of all crystalline phases are observed to decrease, which attest to a gradual transition of the system into a glassy state (Fig. 3). In the stomatological porcelain samples made from such material, shrinkage increases and water absorption decreases in a regular manner with increasing temperature (Table 2).

X-ray phase analysis of the compositions hydroxyapatite – fluorite – potassium feldspar, modified with lithium fluoride to lower the melting temperature (compositions 17 – 19), established that during heat treatment of the initial mate-

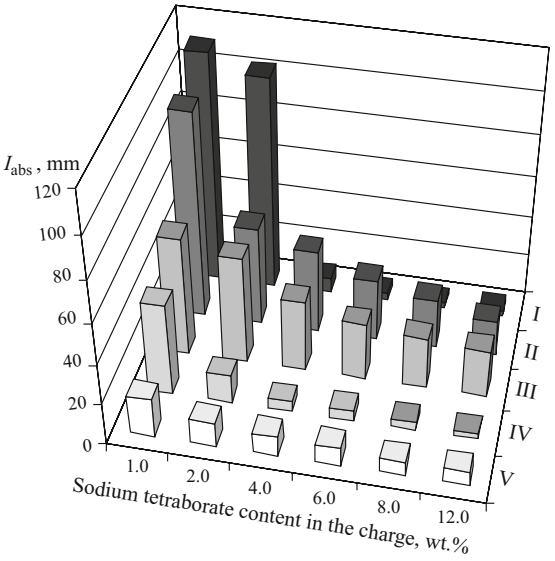

Fig. 3. Change of the intensity of x-ray reflections of different crystalline phases in the finished frit with the composition hydroxyapatite – fluorite – potassium feldspar as a function of the content of the additive sodium tetraborate in the charge (compositions 10 – 15): I) calcium phosphate (d = 0.289 nm); II) wollastonite (d = 0.274 nm); III) fluorapatite (d = 0.279 nm); IV) sodium tetraborate (d = 0.294 nm); V) fluorite (d = 0.193 nm).

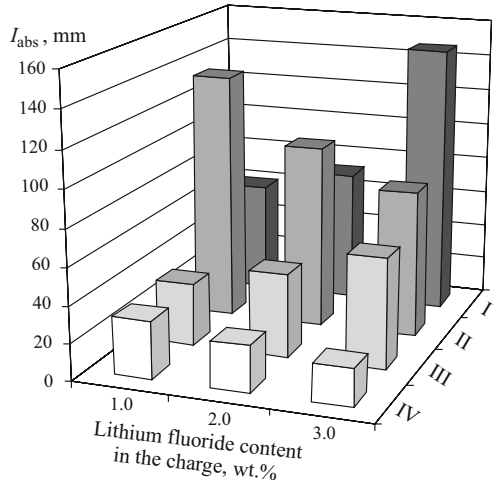

Fig. 4. Change of the intensity of x-ray reflections of different crystalline phases in the finished frit with the composition hydroxyapatite – fluorite – potassium feldspar – LiF as a function of the lithium fluoride content in the charge (compositions 17 – 19): I) fluorapatite (d = 0.279 nm); II) HA (d = 0.281 nm); III) wollastonite (d = 0.274 nm); IV) potassium feldspar (d = 0.299 nm).

rial fluorine ions replace hydroxyl ions in the HA structure, as a result of which the maximum content of fluorapatite increases substantially (Fig. 4).

In pastes containing sodium dihydrophosphate and leucite glass as sintering additive (compositions 20 – 24 and 25 – 29), the main crystalline phase of the materials studied is HA (d = 0.281, 0.271, and 0.226 nm). The intensity of the x-ray reflections from HA decreases with increasing fraction of the sintering additive. In addition, other phases, whose

TABLE 2.

Composition	Component composition of the samples, wt.%	Lineal shrinkage (%) at temperature, °C			Water absorption (%) at temperature, °C		
		900	1000	1100	900	1000	1100
9	15CaF_2 – 78 HA – 7 PF	1	1	1	17.38	16.24	14.25
16	7.5CaF_2 – 51.5 HA – 25 PF – 16$Na_2B_4O_7 \cdot H_2O$	4	4	6	5.00	5.00	2.50
19	7.5CaF_2 – 63.5 HA – 25 PF – 4LiF	3	3	6	1.04	1.00	0.33
20	99 HA – 1 dihydrophosphate		No shrinkage		–	–	13.78
21	97.5 HA – 2.5 dihydrophosphate		Same		–	–	12.64
22	95 HA – 5 dihydrophosphate		″		–	–	11.37
23	92.5 HA – 7.5 dihydrophosphate		″		–	–	8.96
24	90 HA – 10 dihydrophosphate		″		–	–	10.82
25	99 HA – 1 glass		″		–	–	14.07
26	97.5 HA – 2.5 glass		″		–	–	14.81
27	95 HA – 5 glass		″		–	–	15.49
28	92.5 HA – 7.5 glass		″		–	–	15.63
29	90 HA – 10 glass		″		–	–	15.45
30	97.5(CaF_2 – HA) – 2.5LiOH	5	4	4	2.15	2.00	1.60
31	95(CaF_2 – HA) – 5LiOH	5	6	7	2.76	2.36	3.50
32	90(CaF_2 – HA) – 10LiOH	6	7	10	2.78	3.10	3.70
33	85(CaF_2 – HA) – 15LiOH	6	7	11	2.98	3.10	3.90
34	80(CaF_2 – HA) – 20LiOH	6	8	11	3.81	3.50	7.06
35	75(CaF_2 – HA) – 25LiOH	6	8	11	4.53	8.00	8.29

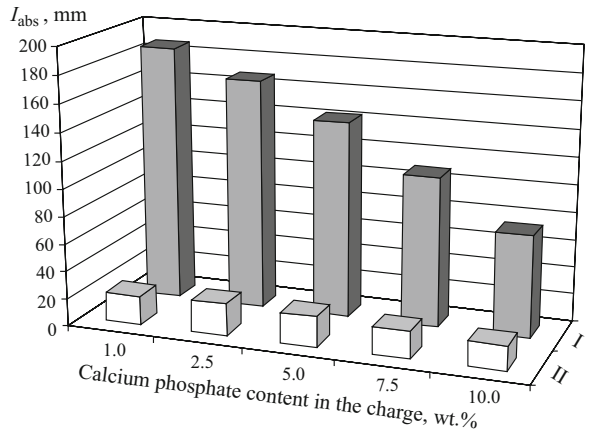

Fig. 5. Change of the intensity of x-ray reflections of different crystalline phases in the finished frit with the composition hydroxyapatite – sodium dihydrophosphate with increasing $NaH_2PO_4 \cdot 2H_2O$ content in the charge (compositions 20 – 24): I) calcium phosphate (d = 0.289 nm); II) HA (d = 0.281 nm).

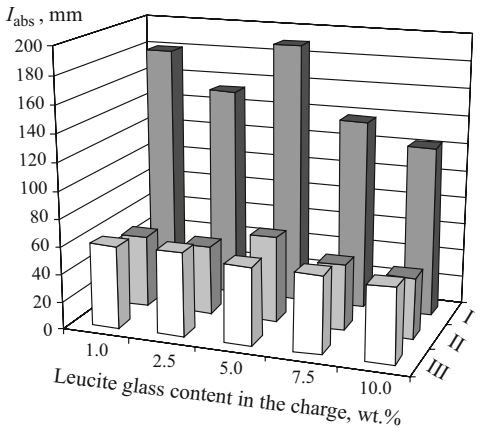

Fig. 6. Change of the intensity of x-ray reflections of different crystalline phases in the finished frit with the composition hydroxyapatite – glass with increasing glass content in the charge (compositions 25 – 29): I) HA (d = 0.281 nm); II) calcium phosphate (d = 0.289 nm); III) leucite (d = 0.325 nm).

composition depends on the form of the additive, are present in some samples: leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$, d = 0.284, 0.239 nm) is identified in the sample containing glass and sodium phosphate (d = 0.261 nm) is identified in the sample containing 10% $NaH_2PO_4 \cdot 2H_2O$. Individual reflections characteristic for calcium phosphate $Ca_3(PO_4)_2$ (d = 0.361, 0.366 nm) are recorded in all x-ray diffraction patterns (Figs. 5 and 6). The material obtained shows no shrinkage (see Table 2). The maximum compression strength of samples with 1.0, 2.5, 5.0, 7.5, and 10.0% dihydrophosphate is 7.54, 17.80, 32.29, 57.94, and 72.2 MPa, respectively. In samples containing 1.0, 2.5, 5.0, 7.5, and 10.0% glass, the strength is 13.26, 13.37, 15.94, 28.18, and 50.03 MPa, respectively.

When the charges with the compositions 30 – 35 are heated, melt already appears at 1150°C. However, as the mixture is heated further, an opaque mass is formed, indicating a possible chemical reaction. The reaction accompanying melting of the charge occurs between LiOH and Ca_3PO_4 with lithium phosphate Li_3PO_4 and free CaO being formed. The intensity of the reaction increases with increase LiOH content. The components react at temperatures above 1150°C. The reaction is accompanied by the transformation of the melt formed into a polycrystalline mixture:

$$6LiOH + Ca_3(PO_4)_2 \rightarrow 2Li_3PO_4 + 3CaO + 3H_2O\uparrow.$$

The presence of free CaO in the samples was checked by White's method [5]. It is precisely the presence of free CaO that explains the nonuniform shrinkage of the samples and the increase of their water absorption. The change in the intensity of the x-ray reflections of the components of the mixture is shown in Fig. 7.

Cylindrical samples 10 mm in diameter and 7 – 10 mm high were made to investigate the properties of the materials

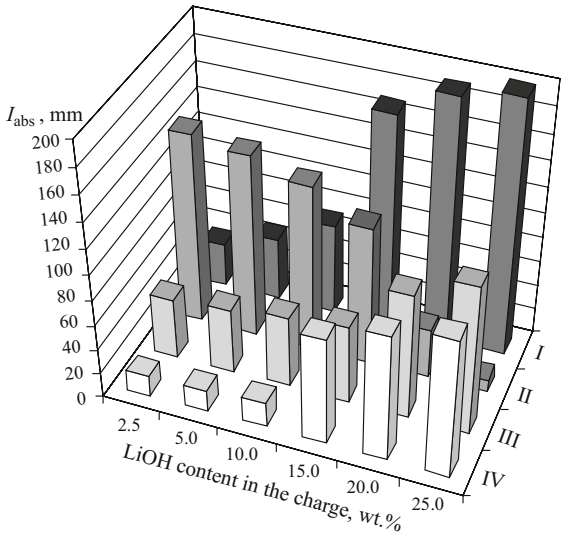

Fig. 7. Change of the intensity of x-ray reflections of different crystalline phases in the finished frit with the composition hydroxyapatite – fluorite as a function of the LiOH additive content in the charge (compositions 30 – 35): I) CaO (d = 0.239 nm); II) HA (d = 0.281 nm); III) $LiCaPO_4$ (d = 0.266 nm); IV) Li_3PO_4 (d = 0.397 nm).

obtained from the finished pastes, comminuted to particles with average diameter 60 μm. The samples from a series with a definite composition were sintered at 900, 1000, and 1100°C. Next, the shrinkage and water absorption of the samples prepared in this manner were measured. The averaged results are presented in Table 2. In accordance with GOST R 51735–2001 requirements, the lineal shrinkage during sintering of stomatological materials should not exceed 16%. The materials satisfy the indicated requirements.

In summary, it has been established that at temperatures above 1150°C the system hydroxyapatite – fluorite actively

interacts with additives consisting of alkali-metal compounds.

When HA interacts with lithium hydroxide, a reaction occurs with formation of CaO, which precludes using LiOH in the charge and means that it must be bound up beforehand. It is preferable to use lithium compounds in the form of salts, for example, lithium fluoride.

Sodium dihydrophosphate and leucite glass used as sintering additives in amounts from 1 to 10% makes it possible to obtain sintered material with high strength characteristics, and the strength of the samples increases with increasing additive content.

The composition hydroxyapatite – leucite glass and hydroxyapatite – sodium dihydrophosphate can be recommended for preparing biologically active inserts and implants for replacing damaged bone fragments, and increasing the flux content makes it possible to use these compositions as coatings for the metal frameworks of metalloceramic dentures.

REFERENCES

1. L. A. Ivanchenko, N. D. Pinchuk, A. A. Krupa, and T. I. Fal'-kovskaya, "Structure and properties of composite materials based on hydroxyapatite," *Steklo Keram.*, No. 6, 30 – 31 (2003).
2. A. Yu. Malysheva, B. I. Beletskii, and E. B. Vlasova, "Structure and properties of composite materials for medical use," *Steklo Keram.*, No. 2, 28 – 30 (2001).
3. T. A. Khabas, E. A. Kulinich, and V. I. Vereshchagin, "Development and investigation of crystal – glass coatings containing hydroxyapatite," *Steklo Keram.*, No. 4, 34 – 36 (2007).
4. E. A. Kulinich, T. A. Khabas, T. V. Nikitina, and A. Nikitina, "Investigation of the sintering of compositions based on hydroxyapatite," in: *Proceedings of the All-Russia Scientific and Applications Conference on New Technologies for Producing and Using Bioceramics in Reconstructive Medicine* [in Russian], Izd. Tomsk. Politekh. Univ., Tomsk (2007), pp. 61 – 66.
5. Yu. M. Butt and V. V. Timashev, *Practical Work in the Chemical Technology of Binding Materials* [in Russian], Vyssh. Shkola, Moscow (1973).